NGR 44-033-007

AIAA Rejected

To 7N

SHORT COMMUNICATION

Matrix effects of iron and nickel in aqueous solutions and powdered samples in X-ray fluorescence spectrometry

IVORY V. NELSON and CHARLES E. URDY

Department of Chemistry, Prairie View A&M College, Prairie View, Texas 77445 (U.S.A.)

Tertian[1] has shown that, for certain solid solutions, the fluorescent intensity Y for a given element and the concentration X of the sample in the flux or the solvent are connected by a simple relationship:

$$Y = \frac{X}{1 + \phi X}$$

where Φ is a matrix factor characteristic of the sample to be analyzed dissolved in a given flux for the required element. It follows that two Y measurements at two different concentrations of X, make it possible to calculate the matrix effect.

Tertian[1] assumed that a series of unknown samples can be prepared so that the matrix factor for element A in the unknown is the same as for the standard. For the unknown intensity measurements, the following equations were then valid:

$$K_A = \left[\frac{1}{\alpha} \frac{(C_n - C_1)}{(C_n \cdot C_1)} \right] \left[\frac{(Y_n \cdot Y_1)}{(Y_n - Y_1)} \right] \tag{1}$$

$$\%A = \frac{100}{H} \left[\frac{(C_n - C_1)}{(C_n \cdot C_1)} \right] \left[\frac{(Y_n \cdot Y_1)}{(Y_n - Y_1)} \right] \tag{2}$$

Thus, theoretically, for the determination of element A in a sample, only two measurements are required on a standard sample for the calculation of K_A from eqn. (1), and two measurements are needed on the unknown for the calculation of A% from eqn. (2). However, in practice, series of standards and unknown samples are prepared and in this case eqns. (1) and (2) can readily be programmed for computer use. A typical computer program for such calculations written in Fortran IV for an IBM 1401 computer, can be obtained from the authors on request.

A report of the application of the Tertian method to aqueous solutions and simple powdered samples is given in this communication.

Sample preparation

Solutions. All stock solutions were made up as *ca.* 8% salt solutions where possible. Standard solutions were made from primary standards or from samples

carefully analyzed here or in commercial laboratories. Solutions for analysis were made by successive dilution of the stock solutions to 0.02% with calibrated pipettes. All solutions were analyzed in liquid cells 1 cm deep and 3 cm in diameter, covered with thin mylar film.

Solids. All solid samples were ground to a powder with a mortar and pestle or in a Spex-800 Mixer-Mill. Samples and borax were ground to pass through a 200-mesh sieve, weighed accurately and mixed thoroughly in the Spex Mixer-Mill. The powders were then pressed into $1\frac{1}{4} \times \frac{1}{8}$ in tablets at 30,000 p.s.i. Powdered samples were made at a concentration of 5% by weight of sample to borax and successively diluted with borax to 0.02%.

Fluorescence analysis

Equipment. All measurements were made on a General Electric XRD-5 X-ray fluorescence spectrometer equipped with a G.E. SPG-3 detector system. For the heavy metal analyses, a scintillation detector, LiF crystal and air path were used. The spectrometer was equipped with a helium tunnel assembly, a PET crystal was available and a flow proportional counter could readily be added for analysis of lighter elements.

Procedure. All analyses were carried out with a tungsten target tube operated at 50 kV and 25 mA. Complete fluorescence spectra of the standard and unknown were initially recorded in order to determine if interfering elements were present, to choose the analytical peak, and to decide how the background was to be measured. For the elemental analysis reported, the analytical peaks were: for iron, FeK α at 57.59° 2θ, and for nickel, NiK α at 48.73° 2θ. The background measurements were made at $+2°$ 2θ (59.59°) for iron and at $-2°$ 2θ (46.73°) for nickel. Peak and background intensities were measured by the stationary crystal–stationary counter method (peak heights). All measurements were for 100-s intervals in order to accumulate a minimum of *ca.* 10,000 counts. The standard counting error was therefore 1% or less. Some typical counting results are shown in Table I.

TABLE I

COUNTING RESULTS OF IRON PRIMARY STANDARD

$(Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O; 99.63\%$ pure)

Sample	Sample concentration (% by weight)	Peak intensity (counts/100 s)	Background intensity (counts/100 s)	Net intensity
1	0.022	12690	9010	3680
2	0.031	13660	8590	5070
3	0.062	18310	9350	8960
4	0.124	24620	9750	14870
5	0.248	37390	9060	28330
6	0.496	60490	8740	51750
7	0.992	108840	8760	100080
8	1.984	194750	8960	185790
9	3.968	334790	8460	326330
10	7.935	521920	8350	513570

Choice of sample type

It was decided to attempt to apply the method of Tertian first to aqueous solutions, because such applications have not been reported previously, and because dilute aqueous solutions of many of the substances under consideration can be readily made. Secondly, attempts were made to apply the method to powdered samples, because, again, such applications have not been reported previously; moreover a diluent of low atomic weight, borax, is readily available, sample preparation is rapid and simple, and found in most analytical laboratories. Most samples that cannot be treated as aqueous solutions, can be readily powdered.

Determination of the optimal concentration range

Table II shows the computation of the matrix and proportionality factor (K from eqn. 1) for an iron standard. The stock solution was made by dissolving 10.5153 g of iron(II) ammonium sulfate hexahydrate (99.63% pure) in 100.0 ml of water and 20.0 ml of 6.0 M hydrochloric acid. The larger values of K for the more dilute solutions can be attributed to the failure of such dilute solutions to provide an "infinitely thick" sample under the conditions of the measurements. Because the last five values of K were nearly constant, the computation was repeated for only those samples; the results are shown in Table III. The optimal concentration for iron in this case is thus seen to be above 0.07%.

TABLE II

COMPUTATION OF MATRIX AND PROPORTIONALITY FACTOR K BY MEANS OF $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$

Sample no.	Sample concentration (% by weight)	%Fe	$K (\cdot 10^{-7})$
1	0.022	0.002	---
2	0.031	0.004	3.21
3	0.062	0.009	2.20
4	0.124	0.018	2.00
5	0.248	0.035	1.85
6	0.496	0.070	1.79
7	0.992	0.141	1.76
8	1.984	0.281	1.74
9	3.968	0.563	1.73
10	7.935	1.126	1.73

The optimal concentration range for the unknown can be established similarly. Since the percentage of the element is calculated with an average K value, the variation in values is independent of the correctness of the K value although the magnitude is not. Table IV shows the calculation of the percent iron in an iron(III) nitrate solution where the K value used was too high.

When the correct percentage of the required element is not known, the optimal concentration range can still be established as the range in which the variation does not exceed the tolerances desired. In this case the error will be less than 3% if the

TABLE III

CALCULATION OF FACTOR K WITH $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$

Sample	Sample concentration (% by weight)	%Fe	K ($\cdot 10^{-6}$)
6	0.496	0.070	—
7	0.992	0.141	7.62
8	1.984	0.281	7.65
9	3.968	0.563	7.65
10	7.935	1.126	7.67
		Average $K = 7.65 \cdot 10^6$	

TABLE IV

CALCULATION OF PERCENT IRON IN ORIGINAL SAMPLE FROM A CALCULATED K VALUE

Sample no.	Sample concentration (% by weight)	%Fe in original sample (calculated from eqn. 2)
1	0.02	—
2	0.03	21.10
3	0.07	14.86
4	0.14	12.95
5	0.28	12.20
6	0.55	11.82
7	1.11	11.62
8	2.22	11.52
9	4.44	11.47
10	8.88	11.44
	Measured % Fe = 13.82	

sample concentration is greater than about 0.5% by weight (an iron concentration of not less than 0.08%).

The optimal concentration range was determined as described above for all standards and unknowns. This procedure required about 35 min for each sample. However, once the range had been established, it was only necessary to run 2–5 samples in all subsequent analyses of the same or similar samples; this reduced the time to 5–15 min per sample. In many cases, instrumental adjustments can be made, so as to reduce the counting time significantly, and the total analysis time is then further reduced.

Analysis of iron solutions

The results obtained for several iron-containing salt solutions are shown in Table V. The salt solutions were prepared by dissolving *ca.* 10 g of the salt in 100.00 ml of water and 20.0 ml of 6 *M* hydrochloric acid. The iron standard used was that shown in Table III ($K_{av} = 7.65 \cdot 10^6$).

TABLE V. CALCULATION OF PERCENT IRON IN VARIOUS IRON SAMPLES

Sample no.	Sample concentration (% by weight)	% Iron found	True % iron	Average error (%)
$Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$				
1	0.49	—		
2	0.98	13.87		
3	1.96	14.22		
4	3.93	14.26		
5	7.86	14.34		
	Average % iron	14.17	14.19	0.14
$Fe(NO_3)_3 \cdot 9H_2O$				
1	0.55	—		
2	1.11	13.75		
3	2.22	13.79		
4	4.44	13.57		
5	8.88	13.56		
	Average % iron	13.67	13.82	0.109
$Na_2Fe(CN)_5NO \cdot 2H_2O$				
1	0.49	—		
2	0.99	18.62		
3	1.98	18.72		
4	3.96	18.65		
5	7.91	18.71		
	Average % iron	18.67	18.74	0.37
Iron ore (Thorn Smith sample #165) in solution				
1	0.06	—		
2	0.13	47.64		
3	0.26	42.00		
4	0.52	41.70	40.56	—
Iron ore (Thorn Smith sample #165) as solid				
5	0.26	—		
6	0.95	40.03		
7	2.41	40.50		
8	4.82	40.94		
	Average % iron	40.49	40.56	—
Iron ore (Thorn Smith sample #173) in solution				
1	0.06	—		
2	0.13	24.94		
3	0.25	23.07		
4	0.50	22.20	18.53	—
Iron ore (Thorn Smith sample #173) as solid				
5	0.27	—		
6	0.83	18.28		
7	2.39	18.53		
8	4.45	18.70		
	Average % iron	18.50	18.53	—

Table V also shows the results for two solutions of iron ores. Because of the low solubilities of these ores, the concentrations were limited to the equivalent of 0.5 g of sample in 100.0 ml of water and 20.0 ml of 6 M hydrochloric acid. The results are obviously poor, undoubtedly because of the low concentration of the solutions. It was not practicable in this particular case to prepare more concentrated solutions, and the possibility of using deeper sample holders was not examined. Since the samples were available as powdered solids that could readily be ground into finer powders, they were therefore analyzed in this manner.

Analysis of iron ores as solids

Unknown samples and standards were prepared as previously described. The standard had a K_{av} value of $5.34 \cdot 10^6$. The results of the analysis of two samples are also shown in Table V. It is probably somewhat fortuitous that the average values are so close to the true values, but the analysis is probably accurate to within 1%.

Analysis of solutions containing both iron and nickel

Solutions containing both iron and nickel were analyzed to determine if the enhancement effect by the nickel K_x line on the iron K line would be effectively compensated for by the Tertian procedure. The samples were also analyzed for nickel content. The standard used for the iron analysis was the same as that used above, *i.e.* $K_{av} = 7.65 \cdot 10^6$. The nickel standard solutions were analyzed solutions of nickel nitrate ($K_{av} = 2.42 \cdot 10^7$). The solutions for analysis were made from a mixture of iron(III) nitrate and nickel(II) nitrate salts. The results of these analyses (Table VI) were less satisfactory than the previous ones, but there was no evidence of enhancement effects.

TABLE VI

CALCULATION OF PERCENT NICKEL AND IRON IN STANDARD UNKNOWN SAMPLES

Sample	Sample concentration (% by weight)	% Iron	% Nickel
1	1.22	—	—
2	1.52	7.65	9.17
3	2.03	7.47	8.91
4	3.05	7.63	8.88
	Average %	7.58	8.99
	True %	7.89	8.68

Conclusion

In the analyses discussed, the Tertian method is applicable to simple aqueous solutions and powdered samples; it is also shown to be simple from the computational point of view. In general, the method seems to be significant enough to justify further study. There are two main areas in which further study might be concentrated: first, a wide range of substances, both in solution and solid states, should be studied in order to establish the general applicability of the method, and, secondly very

dilute solutions should be examined. In this respect, attempts are being made to apply this method to the analysis of biologically important solutions, in particular, the determination of iron in blood.

REFERENCE

1 R. Tertian, *Spectrochim. Acta*, 23B (1968) 305.